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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES
hereby certify that annexed is a true copy of the Provisional specification in
connection with Application No. PQ 0015 for a patent by CAST CENTRE PTY
LTD filed on 28 April 1999.



WITNESS my hand this
Fifteenth day of May 2000

K Ward

KAY WARD
TEAM LEADER EXAMINATION
SUPPORT AND SALES

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PROVISIONAL SPECIFICATION

Invention Title: **GASEOUS COMPOSITIONS**

The invention is described in the following statement:

GH REF: P50352CN/PJW

FIELD OF THE INVENTION

The present invention relates to gaseous compositions and, more particularly, to gaseous compositions useful as cover gases for protecting molten magnesium/magnesium alloys. The present invention also relates to a method for protecting molten magnesium/magnesium alloys and to a method for extinguishing magnesium/magnesium alloy fires.

BACKGROUND ART

Magnesium is a highly reactive and thermodynamically unstable element. Molten magnesium is readily and violently oxidised in ambient air, burning with a flame temperature of approximately 2820°C. Three approaches have been used to inhibit the severe oxidation process. Salt cover fluxes may be sprinkled over the molten metal; oxygen may be excluded from contacting the molten metal by blanketing the molten metal with an inert gas such as helium, nitrogen or argon; or a protective cover gas composition may be used to blanket the molten metal. Protective cover gas compositions typically comprise air and/or carbon dioxide and a small amount of an inhibiting agent which reacts/interacts with the molten metal to form a film/layer on the molten metal surface which protects it from oxidation. The mechanism by which inhibiting agents protect molten reactive metals is not well understood.

Prior to about the mid-1970's, sulphur dioxide (SO_2) was widely used as an inhibiting agent in a magnesium cover gas composition but was replaced by sulphurhexafluoride (SF_6) which has become the industry standard. Typically, SF_6 based cover gas compositions contain 0.2-1% by volume SF_6 and a carrier gas such as air, carbon dioxide, argon or nitrogen. SF_6 has the advantages that it is a colourless, odourless, non-toxic gas which can be used in the production of bright and shiny ingots with relatively low dross formation. However, SF_6 suffers from several disadvantages. Its sulphur based decomposition products at high temperature

are very toxic. It is expensive and has limited sources of supply. It is one of the worst known greenhouse gases having a Global Warming Potential (GWP) at a time horizon of 100 years of 24,300 relative to carbon dioxide.

5 It is also noted that once magnesium has ignited, the resulting fire cannot be extinguished even with high concentrations of SF_6 . SO_2 is even worse in this respect as it can accelerate a magnesium fire. The only known cover gas for extinguishing a magnesium fire is boron trifluoride which is very expensive and very toxic.

10 Alternative cover gas compositions are desirable.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a cover gas composition for protecting molten
15 magnesium/magnesium alloy, the composition including a hydrofluorocarbon.

The composition may include a mixture of hydrofluorocarbons and preferably comprises a minor amount of hydrofluorocarbon(s) and a major amount of a
20 carrier gas. More preferably, the composition consists of less than 1% by volume hydrofluorocarbon(s) and the balance carrier gas. Preferably, the hydrofluorocarbon(s) have GWP's (referenced to the absolute GWP for carbon dioxide at a time horizon of 100
25 years) of 5000 or less and no component of the composition has a GWP greater than 5000.

Suitable carrier gases include air, carbon dioxide, argon, nitrogen and mixtures thereof.

Suitable hydrofluorocarbons are listed in Table 1
30 below which includes their GWP's (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) which have been sourced from IPCC 1996.

TABLE 1

Hydrofluorocarbon	Industry Name	Formula	GWP
difluoromethane	HFC-32	CH_2F_2	650
pentafluoroethane	HFC-125	C_2HF_5	2,800
tetrafluoroethane	HFC-134a, R134a	$\text{C}_2\text{H}_2\text{F}_4$	1,300
difluoroethane	HFC-152a, R152a	$\text{C}_2\text{H}_4\text{F}_2$	140
heptafluoropropane	HFC-227ea	C_3HF_7	2,900

In a second aspect, the present invention provides a method of protecting molten magnesium/magnesium alloy, the method including blanketing the molten magnesium/magnesium alloy with a cover gas composition according to the first aspect of the present invention.

The method according to the second aspect of the present invention is applicable to protecting molten magnesium/magnesium alloy in a foundry vessel such as a furnace and during casting.

In a third aspect, the present invention provides a method for extinguishing a magnesium/magnesium alloy fire, the method including subjecting the fire to a flow of hydrofluorocarbon(s).

EXAMPLES

Example 1

A furnace containing 20kg of molten magnesium at 700°C was blanketed with gaseous compositions consisting of 0.3% by volume tetrafluoroethane and the balance (a) dry air, (b) moist air, and (c) carbon dioxide. In each of the three trials hydrogen fluoride levels were monitored using Drager tubes. Good molten magnesium protection was observed in each of the trials with hydrogen fluoride levels of 30-70ppm detected. The choice of carrier gas was not observed to noticeably affect the level of hydrogen fluoride produced.

Comparative Example 1

Comparative Example 1 was identical to Example 1 with the exception that tetrafluoroethane was replaced by

SF₆. Good molten metal protection was observed in each of the three trials and similar levels of hydrogen fluoride were detected.

5 Example 1 and Comparative Example 1 demonstrate that the inventive gaseous compositions provide equivalent melt protection to SF₆ based compositions with no greater production of hydrogen fluoride.

Example 2

10 A series of single ingots of both pure magnesium and magnesium-aluminium alloy AZ91 were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a
15 cover gas composition, and the molten metal was allowed to solidify. In the case of AZ91 alloy the cover gas composition consisted of 0.04% by volume tetrafluoroethane and the balance dry air. The cover gas composition for the pure magnesium casting consisted of
20 0.1% by volume tetrafluoroethane and the balance dry air. Hydrogen fluoride production was monitored during casting using Drager tubes and no hydrogen fluoride was detected.

Single ingots of both pure magnesium and AZ91 alloy were produced free of burning, with bright shiny surface
25 finishes, with very low levels of dross, and with no reaction with boron nitride mould coatings.

Comparative Example 2

Comparative Example 2 was identical to Example 2 with the exception that tetrafluoroethane was replaced by
30 SF₆.

The ingots produced in Example 2 had lower levels of dross and were more attractive than those produced in Comparative Example 2.

Example 3

35 Molten magnesium was ignited and the resulting magnesium fire was subjected to a flow of pure tetrafluoroethane which extinguished the fire quite quickly.

Comparative Example 3

Comparative Example 3 was identical to Example 3 with the exception that tetrafluoroethane was replaced by SF_6 .

5 The pure SF_6 was incapable of extinguishing the magnesium fire.

DATED this 28th day of April 1999

CAST CENTRE PTY LTD

By its Patent Attorneys

10 GRIFFITH HACK